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Participation of a Chain Mechanism in Efficient Monomerization of Dimethylthymine Cyclobutane Dimer Photosensitized by a Flavin in the Presence of Perchloric Acid

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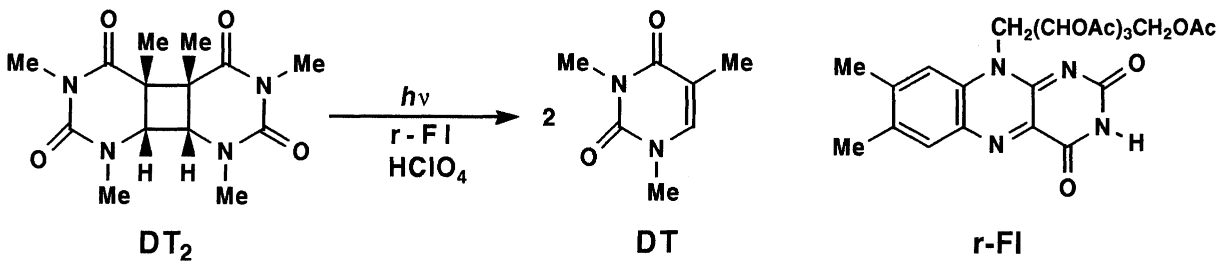
The monomerization of *cis-cisoid* cyclobutane dimer of 1,3-dimethylthymine is photosensitized by riboflavin tetraacetate with quantum yields of larger than unity in Ar-purged solution in the presence of perchloric acid, whereas the limiting quantum yields for degassed and aerated solutions are unity.

Enzymatic photorepair of UV-damaged DNA occurs through the monomerization of pyrimidine dimers under irradiation at > 300 nm,1) which is believed to involve electron transfer between dimers and photoexcited chromophore(s) of photolyase,2) as revealed by extensive studies on photosensitized monomerization of dimer models by a variety of photosensitizers.3,4) Recently, the chromophores of photolyases in some biological systems have been identified as reduced FAD,5) a pteridine,6) and a 5-deazaflavin.7) However, model photoreactions using a variety of flavin photosensitizers are very inefficient ($\phi \leqq 10^{-2}$)8-10) unlike enzymatic photorepair. We found that the photosensitized monomerization of *cis-cisoid* 1,3-dimethylthymine cyclobutane dimer (DT_2) by riboflavin tetraacetate (r-Fl) and a 5-deazaflavin derivative does efficiently proceed only in the presence of $Mg(ClO_4)_2$ or $HClO_4$ ($\phi^{\infty} \cong 1.0$) through electron transfer from DT_2 to the triplet flavins complexed with Mg^{2+} or to *both* the excited-singlet and triplet states of the protonated flavins.11) In this communication, we wish to report the *participation of a chain-reaction pathway* as another mechanistic channel in the r-Fl-photosensitized monomerization of DT_2 in the presence of perchloric acid.



As is shown in Fig. 1, quantum yields for Ar-purged solution (ϕ(Ar)) exceed unity at $\geq$ 0.03 M (1 M = 1 mol dm^{-3}) in DT_2, demonstrating the participation of a chain-reaction mechanism. On the other hand, the limiting quantum yields for degassed and aerated solutions are commonly unity.[11] Quenching of the monomerization by 1,2,4-trimethoxybenzene (TMB) occurred to give a Stern-Volmer plot with a break at $\approx 10^{-3}$ M in TMB (Fig. 2), indicating the involvement of two or more reactive species. A double-reciprocal plot of ϕ(Ar) *vs.* $[DT_2]$ for Ar-purged solution in the presence of 8 x 10^{-4} M TMB is linear with an intercept-to-slope ratio of 23 M^{-1}, which is in good agreement with the Stern-Volmer constant (28 M^{-1}) for quenching of r-Fl fluorescence by DT_2; at

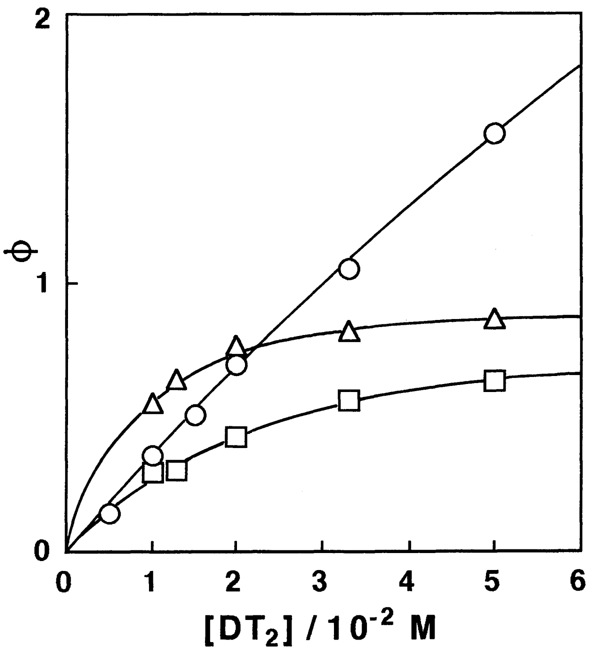


Fig. 1. Dependence of monomerization quatum yields on DT_2 concentration for Ar-purged (- ○ -), degassed (- △ -), and aerated (- □ -) acetonitrile solutions at 30 °C; [r-Fl] = 0.5 mM and $[HClO_4]$ = 10 mM; irradiation at 366 nm.

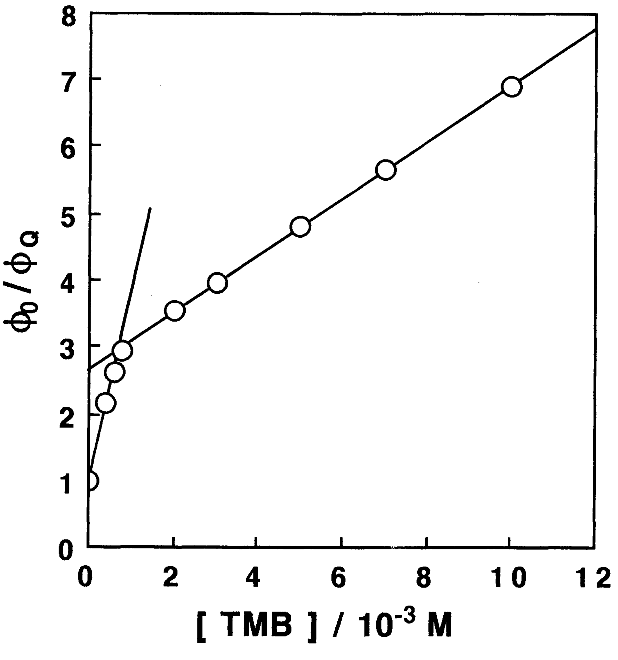
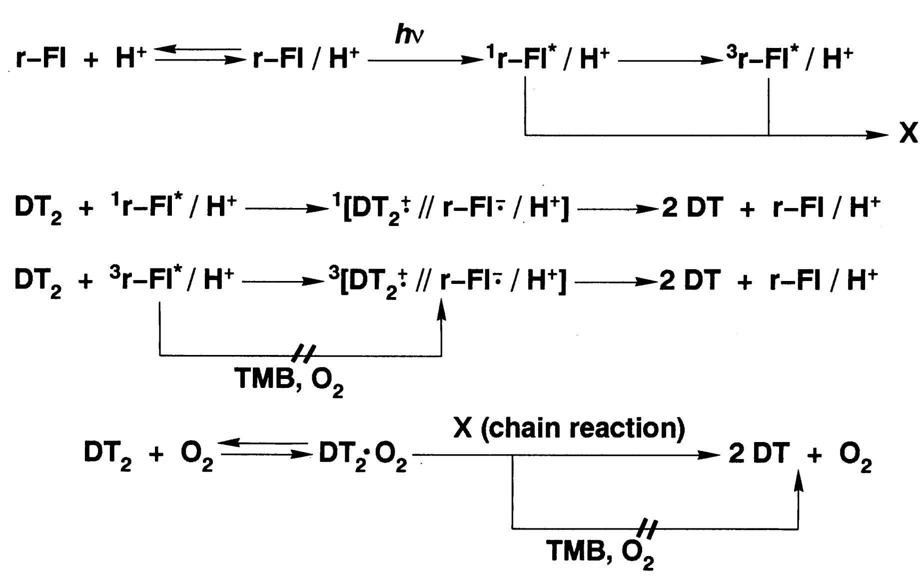


Fig. 2. A Stern-Volmer plot for quenching of the photosensitized monomerization of DT_2 by 1,2,4-trimethoxybenzene (TMB) in Ar-purged acetonitrile solution at 30 °C; [r-Fl] = 0.5 mM, $[DT_2]$ = 20 mM, and $[HClO_4]$ = 10 mM; irradiation at 366 nm.

this concentration of TMB, quenching of r–Fl fluorescence is not important ($\approx$ 6 %). The complete interception of both the triplet and chain-reaction pathways should occur by 8×10^{-4}-M TMB to leave only the reaction *via* the excited-singlet state. The limiting quantum yield obtained from the intercept of the plot 0.85, showing that the excited-singlet state of protonated r–Fl can almost quantitatively monomerize DT_2 *via* electron transfer with little geminate recombination of ion-radical pair. Since the limiting quantum yields for degassed and aerated solutions are unity,11) the participation of a chain reaction in degassed and aerated solutions should be only minor.

A crucial question should emerge as to why the participation of a chain reaction is important in Ar-purged solution. In a previous paper,12) we reported that DT_2 forms a complex with O_2 ($DT_2 \cdot O_2$), which is very reactive toward the monomerization catalyzed by the photogenerated cation radical of aromatic hydrocarbons, and that $DT_2 \cdot O_2$ still exists to a substantial extent even after prolonged flushing with pure N_2 or Ar. It is therefore an attractive speculation that only $DT_2 \cdot O_2$ would be responsible for the chain process. However, possible effects of O_2 on the r–Fl-photosensitized monomerization might be critical depending on its concentration, since excess O_2 should scavenge a variety of reactive species competitively with the formation of $DT_2 \cdot O_2$. Flushing of solution with Ar would remove excess O_2 but leave $DT_2 \cdot O_2$ in an amount enough for the chain process to proceed. On the other hand, concentration of O_2 in aerated solution should be high enough for interception of the chain process.

At present, the chain carrier is still unknown. One of the possible species would be the monomer cation radical that must be formed by splitting of the photogenerated $DT_2^{\cdot+}$. However, this



be unlikely, since the photosensitized monomerization of DT_2 by Mg^{2+}-complexed r-Fl under Ar is less efficient than that of degassed solution.11) This is again true in the chloranil-photosensitized monomerization of DT_2.13) Presumably, a reactive species (X) which is yet unknown would be photochemically generated from protonated r-Fl to catalyze the photochemical monomerization of $DT_2{\bullet}O_2$.14) Further investigation including the identification of the reactive species and kinetic analysis is now in progress.

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14) Alternatively, the cation radical of *protonated* dimethylthymine ($DT^{+\bullet}/H^+$) would function as the chain carrier receiving an electron from DT_2.

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